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MEMORANDUM FOR PRS (Contractor Publication)

FROM: PROI (TI) (STINFO) 9 September 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-0176**
Velarde, S.P., et al., (Thiokol) "Synthetic Directions in New Energetic Materials for Advanced Solid Rocket Propellants"

Seventeenth Working Group Mtg. of HEDM **(Statement A)**

16th + 17th Sept AFRL - PR - ED - TP - FY1999 - 0176

Synthetic Directions in New Energetic Materials for Advanced Solid Rocket Propellants

S. P. Velarde, L. F. Cannizzo, T. K. Highsmith, R. S. Hamilton,

W. W. Edwards, R. M. Hajik, M. A. Dewey,

B. A. Zentner, L. R. Huntsman

Submitted in consideration for the Department of the Army Seventeenth Working Group Meeting on Synthesis of High Energy Density Materials

Several programs are currently underway at Thiokol Propulsion which strive to meet or exceed the goals of the Integrated High Performance Rocket Propulsion Technology (IHPRPT) Program. The three major program efforts are: the completed Advanced Oxidizers and Fuels Program, in which was synthesized and evaluated a series of new ingredients for solid rocket propellants; the current Hybrid Fuel Program, which will produce fuels that complement the Tactical Hybrid Rocket Engine Applied Technology (THREAT) Program design and proposed advanced oxidizer; and the current Phase III Ingredient Program, which strives to identify novel, high performance, solid propellant ingredients for boost and orbit transfer applications. All three programs have already undergone down-selection from myriad of possible compounds to a much more workable number of candidates for synthetic consideration.

Based on several factors including: 1) predicted performance of propellant; 2) expected safety properties, thermal stability, and ingredient compatibility; and 3)

ease/cost of synthesis; several furazan based candidates were synthesized for the Alternate Oxidizers and Fuels Program. Five candidates have been targeted for route development in the Hybrid Fuel Program, and at least seven candidates are under investigation in the Phase III Ingredient Program. In the Alternate Oxidizers and Fuels Program aminonitrofurazan (ANF), diaminoazofurazan (DAAF), diaminoazoxyfurazan (DAAOF), dinitroazoxyfurazan, and dinitrobisfurazanopyrazine (PIPER) have all been synthesized from the common precursor diaminofurazan (DAF). The candidates for the Hybrid Fuels are: 4-amino-3,5-dihyrazino-1,2,4-triazole dinitramide (ADHTDN); 1-amino-3,5-dinitro-1,2,4-triazole (ADNT); octahydro-2,5-bis(nitroimino)imidazo[4,5-*d*]imidazole (BNNII); 2,6-dinitraminospiro[3,3]heptane (SPIRO); and tetraazotetrafurazan oxide (TATFO). The Phase III Ingredient candidates include neutral compounds such as: 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HCO); 1,7-diazido-2,4,6-trinitrazaheptane (DAHT); bis[1,1-(3,5-dinitro-1,2,4-triazolo)methyl] nitramine (NBDNT); 1,9-diazido-2,8-dinitraza-5-methylazanonane (DATNN). In addition, several energetic salts remain as possible Phase III Ingredients, including: hydroxyguanidinium and some bis(oxyammonium)nitramine species. The synthesis and some of the relevant safety data of these compounds will be discussed.

Synthetic Directions in New Energetic Materials Research for Advanced Solid Rocket Propellants

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Thiokol Propulsion Group

THIOKOL
PROPULSION GROUP

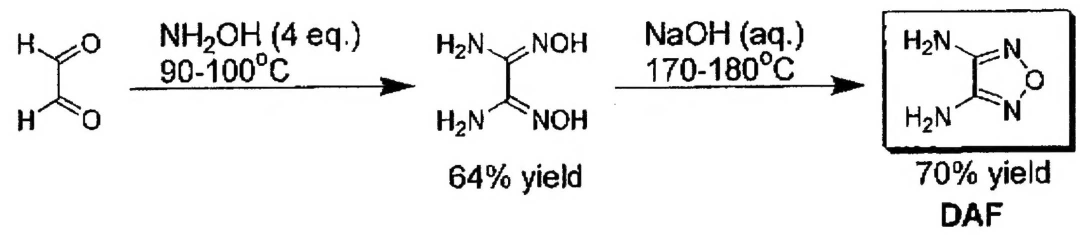
OUTLINE

- ***Integrated High Performance Rocket Propulsion Technology (IHPRPT) Ingredients Synthesis Program at Thiokol***
  - *Alternate Oxidizers and Fuels Program*
    - Synthesis and characterization of program candidates
  - *Hybrid Fuels Program*
    - Tactical hybrid design
    - Program approach
    - Synthesis and characterization of program candidates
  - *Phase III Ingredients Program*
    - Program goals
    - Synthesis and evaluation of program candidates
- ***Conclusions***

IHPRPT Alternate Oxidizers and Fuels Program

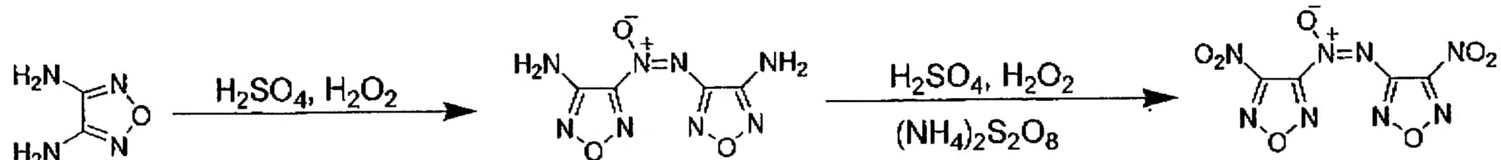
- U.S. technology for producing solid rocket propellants has been optimized during the last 30-40 years
- formulation work has been optimized using the ingredients which give the best performance for a series of different applications
- to meet the goal of increasing the performance of future solid rocket propellants the development of new ingredients for formulation is required
- these new materials must be acceptable for propellant processing and meet additional requirements for low hazards and environmentally-compatible manufacturing and use
- the Integrated High Pay-Off Rocket Propulsion (IHPRPT) Program is designed to coordinated the efforts of government and industry to achieve this goal
- Thiokol has been funded by AFRL under the IHPRPT Alternate Oxidizers and Fuels Program to synthesize and evaluate a series of new ingredients for solid rocket propellants

Synthesis - DAF



- DAF (Zelenin, A. K.; Trudell, M. L. *J. Heterocyclic Chem.* **1997**, *34*, 1057) is the common precursor for DAAOF, DAAF, DNAF, ANF, and PIPER

Synthesis - DAAOF/DNAF

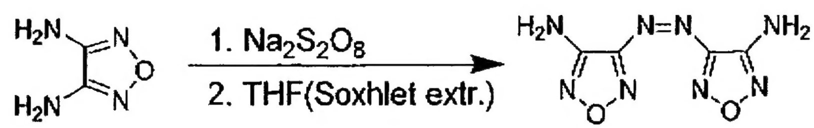


90% yield
DAAOF

50-60% yield
DNAF

- DAAOF first reported in 1981 (Solodyuk, G. D.; et al. *Zh. Org. Khim.* **1981**, *17*, 861.)
- DAAOF exhibits good friction and impact safety characteristics
- DNAF exhibits poor thermal and friction safety properties -- UNSUITABLE FOR FURTHER FORMULATION STUDIES

Synthesis - DAAF

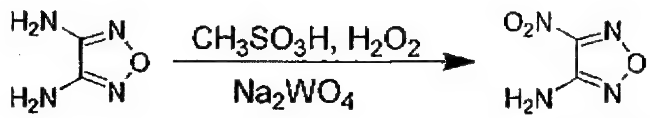


55% yield
DAAF

SAFETY TESTING	RESULT
ABL impact (cm) – TIL	80
ABL friction (psi) – TIL	<u>800@8</u> ft/s
TC ESD (joules) – 50%	0.52
TC confined ESD (joules)	1
SBAT onset (°F)	434
TC impact (inches) – 50%	>46
TC friction (lbs) – 50%	>64

• Gunasekaran, A.; Trudell, M. L.; Boyer, J. H. *Heteroatom Chemistry* **1994**, *5(5/6)*, 441.

Synthesis - ANF

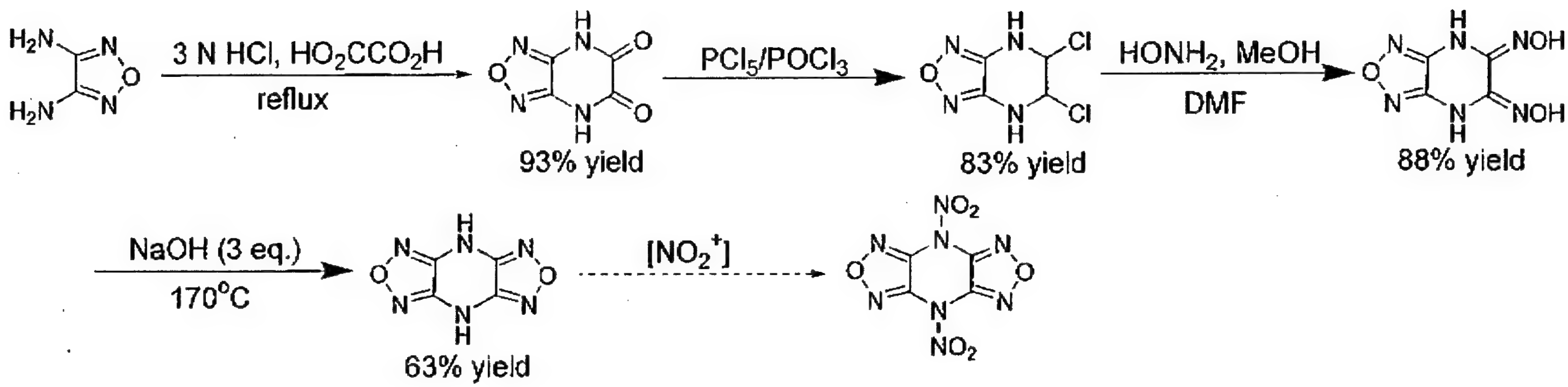


66% yield
ANF

SAFETY TESTING	RESULT
ABL impact (cm) – TIL	11
ABL friction (psi) – TIL	800@8 ft/s
TC ESD (joules) – 50%	1.9
TC confined ESD (joules)	1
SBAT onset (°F)	213
TC impact (inches) – 50%	42
TC friction (lbs) – 50%	>64

- [Schmidt, R. D. (Lawrence Livermore National Laboratory), Private Communication]
- ANF also has undesirable thermal properties (VTS - 100°C, 48 h. >10 ml/g)

Synthesis - PIPER



- PIPER has been a target in the US for a number of years (Fischer, J. W.; et al. *J. Heterocyclic Chem.* **1991**, *28*, 1677).
- nitration step has proven to be the most challenging -- unable to isolate the nitrated product (cf. Tselinskii, I. V.; et al. *Russian Journal of Organic Chemistry* **1997**, *33(11)*, 1656).

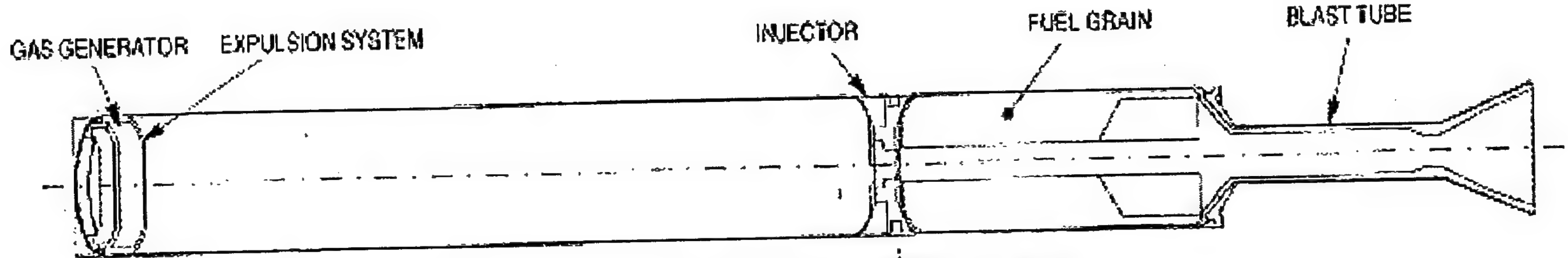
Hybrid Fuels

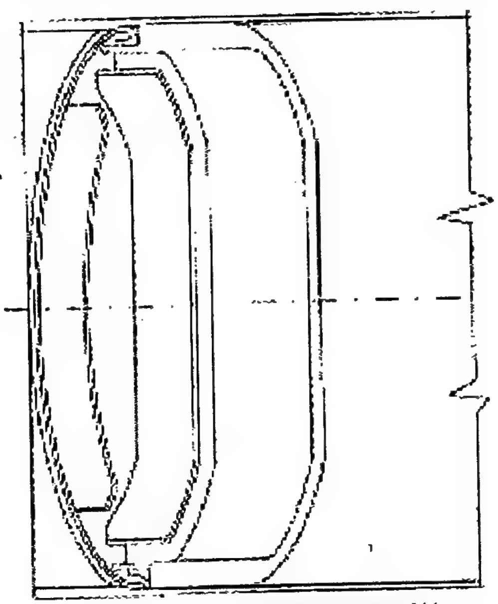
- **Objective - New Energetic Hybrid Fuels (AFRL)**
  - Technical Objective - Develop new energetic ingredients for application in advanced hybrid rocket fuel grains which will help contribute to a significant increase in delivered energy over IHPRPT tactical motor baseline

PROPULSION GROUP

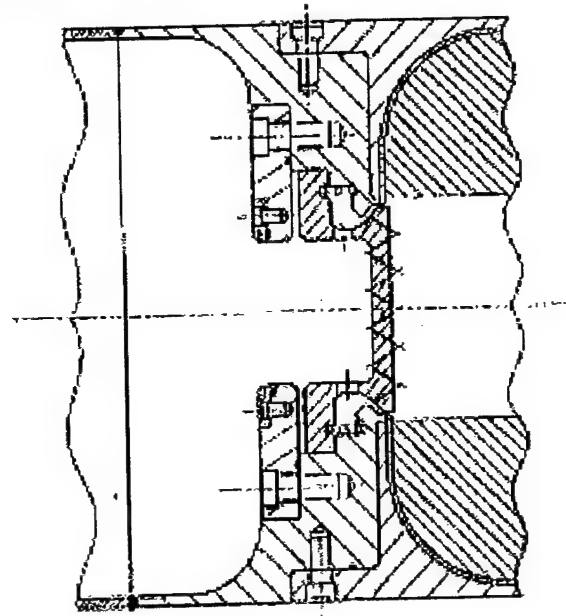
THIOKOL

Tactical Hybrid Approach





ROLLING-BLADDER DIAPHRAGM
WITH INTEGRAL GAS GENERATOR



INJECTOR

Downselection of Candidates

- started with ca. 24 possible targets, and a wide range of molecular moieties (furazans, nitrates and dinitramides, ring-strained hydrocarbons, *gem* dinitro compounds, azoles, and nitroguanidine derivatives)

Performance Calculations

- narrow list of candidates to those which gave >1% increase in del Ivac X density over best baseline material (5-AT; del Ivac X density = 16.91) -- twelve candidates remained

Safety, Thermal Stability, Compatibility

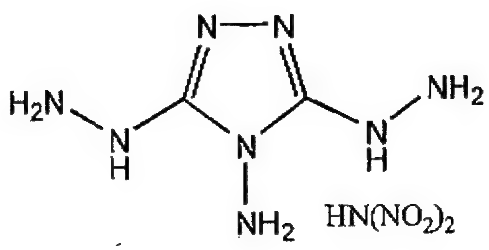
- four candidates were judged to have unsuitable properties for current application

Synthesis

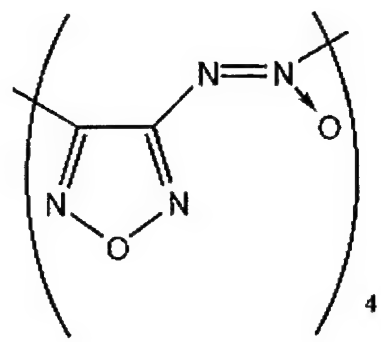
- evaluation of the synthesis of the remaining candidates (current scale, number of steps, overall yield, cost of materials, difficulty) eliminated three candidates

PROPULSION GROUP **THIOKOL**

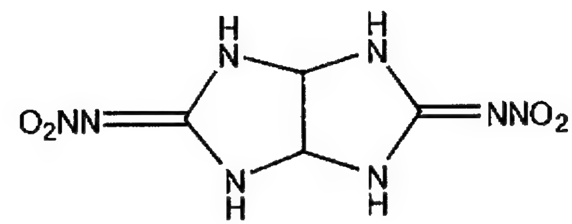
Resulting Five Candidates



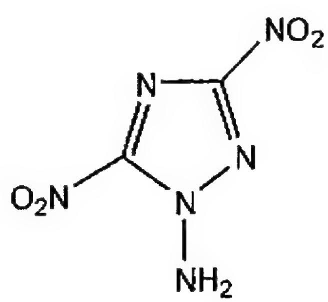
ADHTDN



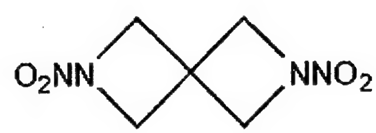
TATFO



BNNII

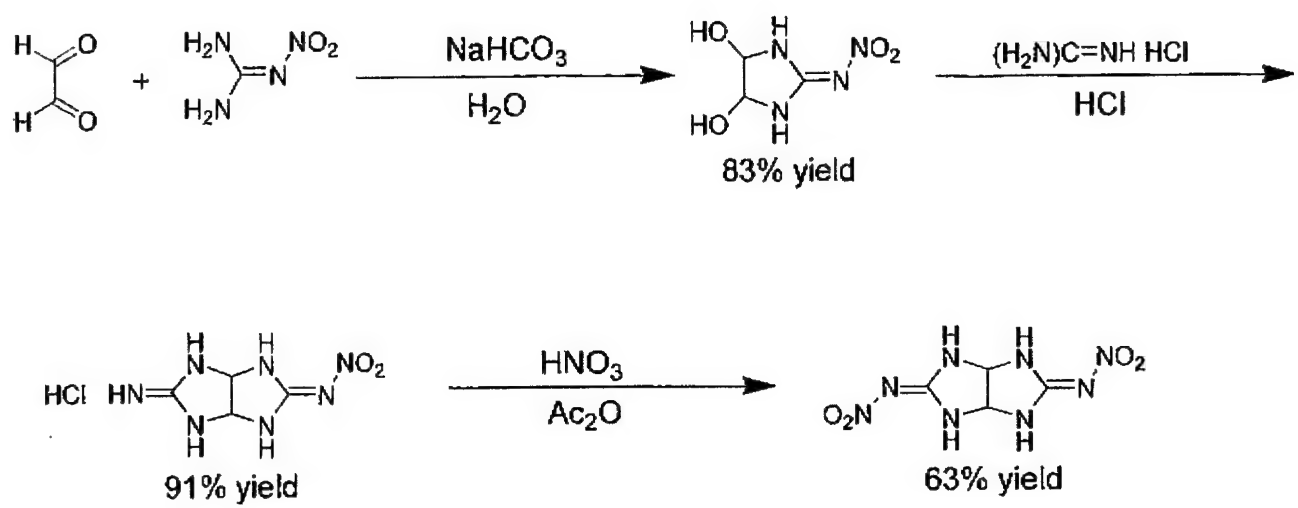


ADNT



SPIRO

Synthesis - BNNII



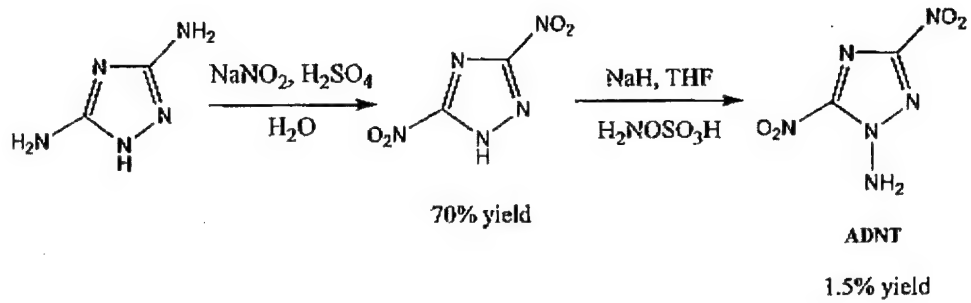
- BNNII synthesized in Australia (Dagley, et al. *J. Energetic Materials* **1995**, *13*, 35).
- simple three step synthesis based upon low cast starting materials
- a one step synthesis based upon nitroguanidine and glyoxal may be feasible

BNNII - Characterization

- material is thermally very stable
  - DSC onset (20°C/min) = 332°C
  - SBAT onset (24°F/hr) = 460°F
  - VTS (120°C, 40 hours) = 0.0 mL gas/gram
- measured density = 1.836 g/cc (X-ray density = 1.84 g/cc)
- measured heat of formation >24 kcal/mole
- excellent small scale safety properties

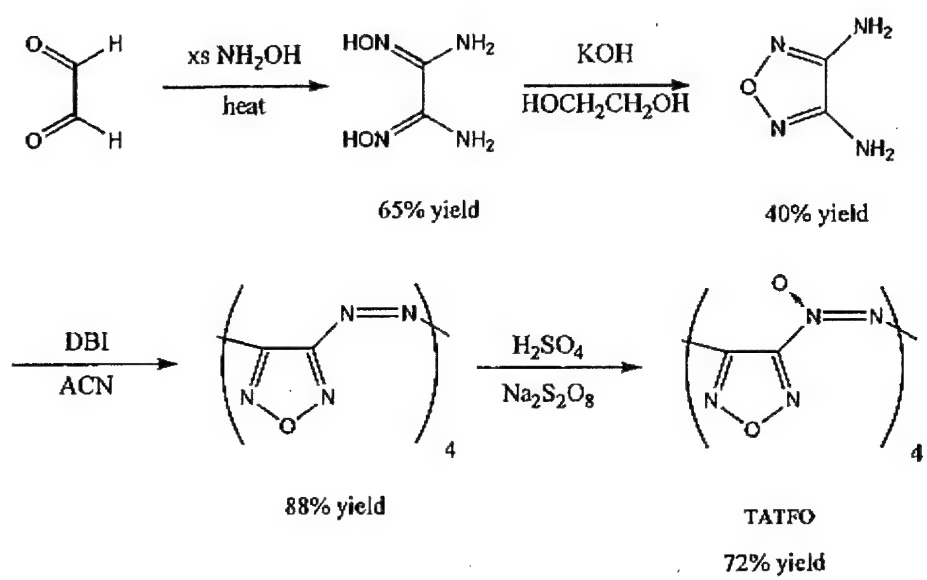
Test	BNNII
SAFETY TESTING	
ABL impact (cm) - TIL	3.5
ABL friction (psi) - TIL	800 @8 ft/s
TC ESD (joules) – 50%	>8
TC confined ESD (j)	8
TC impact (inches) - 50%	>46
TC friction (lbs) - 50%	>64
mini card gap test (0 cards)	NO GO
Russian DDT (500 psi)	NO GO

Synthesis - ADNT



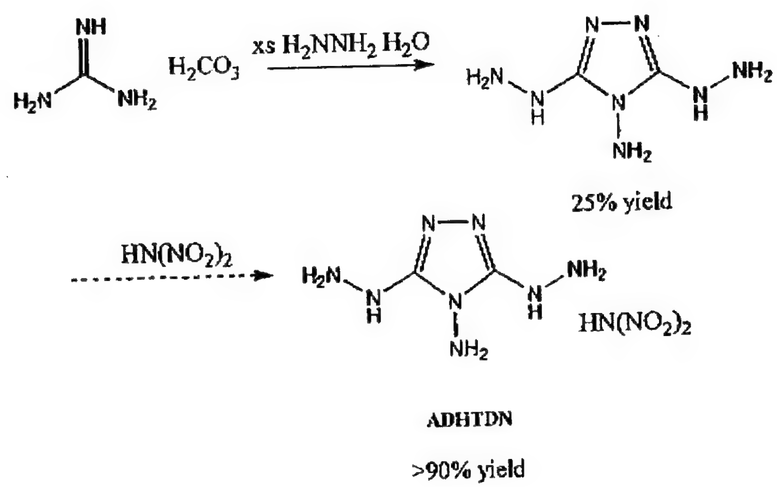
- ADNT has been synthesized at SRI
- first step is known (Steinceifer, M. 9th Det. Symp.)
- second step suffers from low yield (1.5%)
- alternate amination methods will need to be explored
- low cost materials required for synthesis
- low number of steps

Synthesis - TATFO



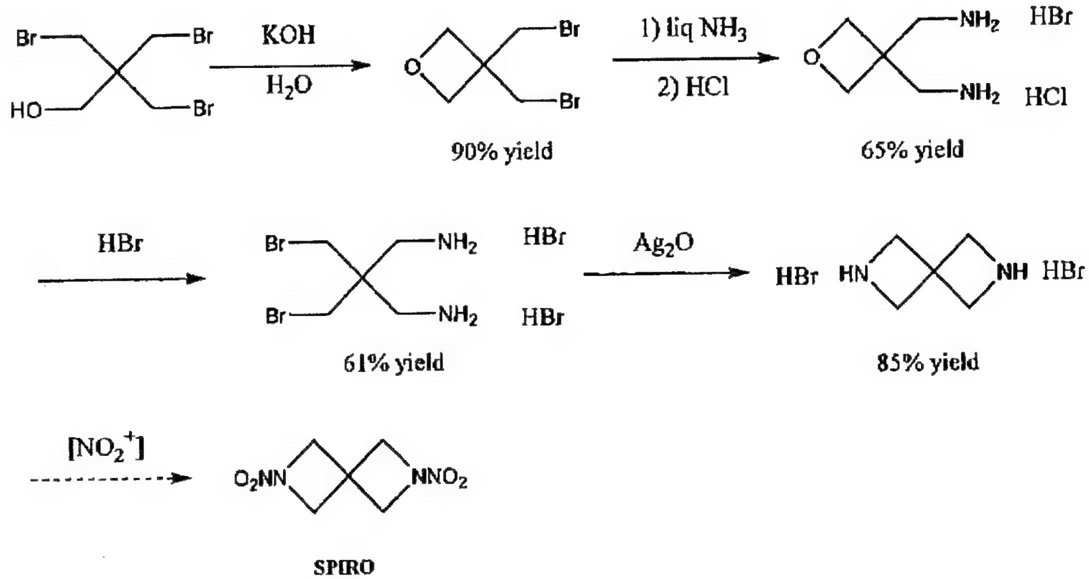
- TATFO recently reported in the literature
  Eman, et al *Mendeleev. Commun*. **1997**, 6.
- intermediate diaminofurazan (DAF) has been made at the multi hundred gram scale at Thiokol
- synthesis uses mostly low cost materials and involves simple reaction conditions and isolation methods
- unfortunately, material is too sensitive to be considered any further for the hybrid fuels program

Synthesis - ADHTDN



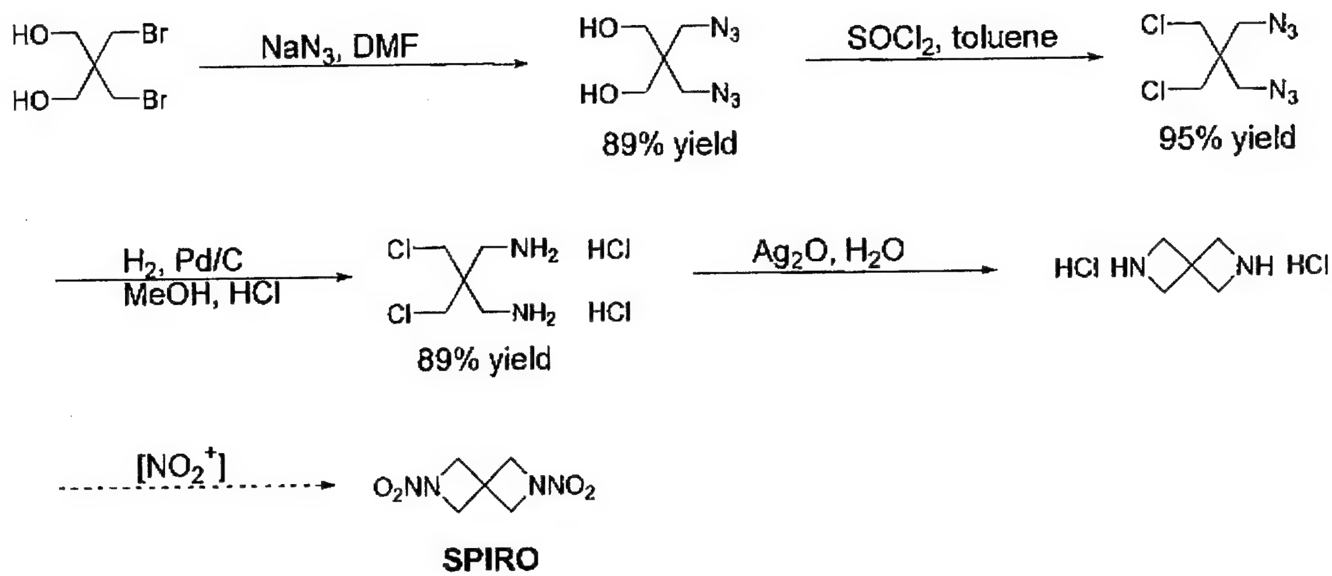
- precursor triazole has been made at Thiokol on a 25 gram scale by a literature method and converted to nitrate salt
  Leonova, et al *Zh. Obsch. Khim*. **1987**, *11*, 2590.
- reaction with dinitraminic acid should give the salt in high yield
- relatively low cost method to make ADN (dinitraminic acid precursor) by Bofors increases synthetic viability of dinitramide salts
- material is too sensitive to consider for hybrid fuels program

Synthesis - SPIRO



- SPIRO conceived by Dr. Suresh Suri of AFRL
- synthesis uncompleted at both AFRL and Thiokol
- proposed route utilizes nitration of known precursor
- nitration of azetidines is precedented (e.g. TNAZ)
- low cost starting materials
- can reasonably propose a two or three step future synthesis

SPIRO Synthesis - Alternate Route

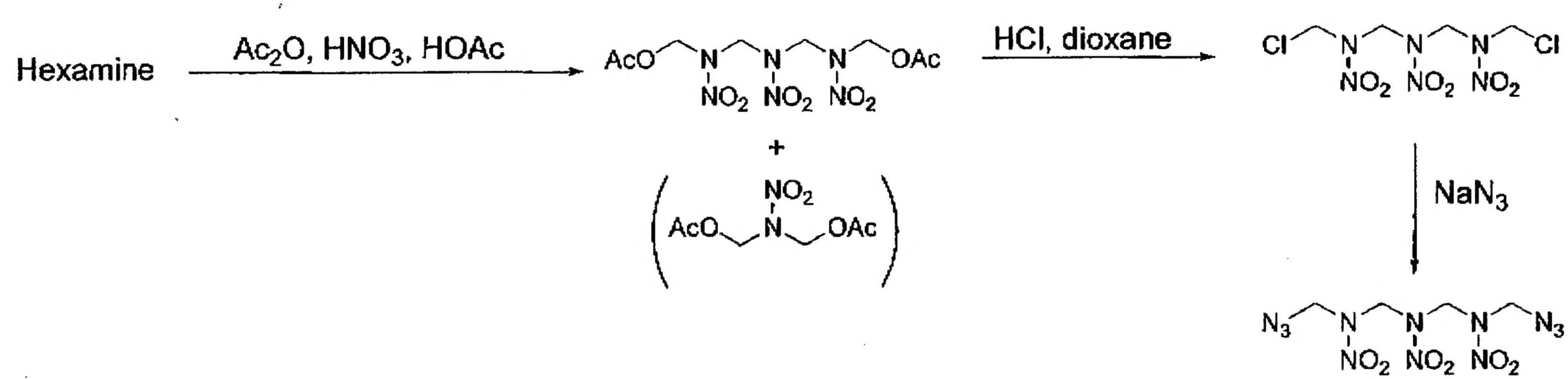


- same number of overall steps as originally proposed SPIRO synthesis
- better stepwise yields

IHPRPT Phase III Solid Propellants Ingredients Program

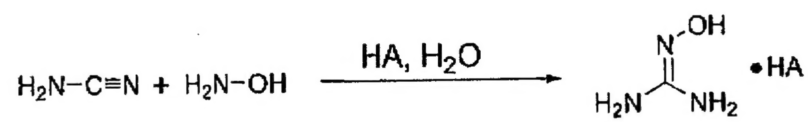
- aimed at the identification and production of new, very high performance, solid propellant ingredients for boost and orbit transfer applications
- goal is to increase Isp (del.) by 12 sec. and increase propellant density by 6%
- target compounds are either already known materials or readily available from known materials (i. e. no new chemical methodology will be developed for the construction of the candidate molecules)
- both energetic neutral molecules, as well as energetic salts, will be surveyed
- the salts will represent a combinatorial type matrix of cations and anions

Synthesis - DATNN



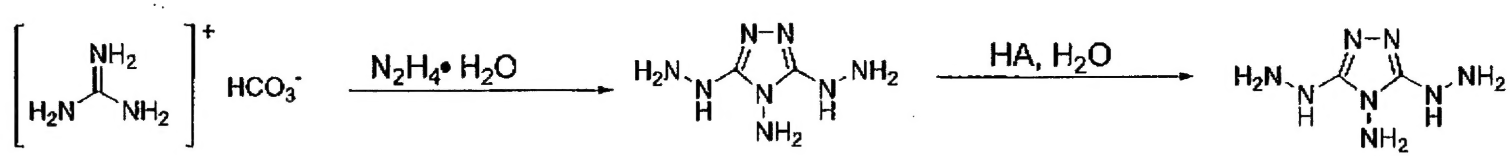
- several grams of the 1,3 acetoxy-2-nitrazapropane derivative was converted to the dichloride (Flannigan, J. E.; Frankel, M. US Patent 4,085,123).

Synthesis - HQ Salts



- salts of HCl and H_2SO_4 are known (Taylor, P. J.; Wait, A. R. *J. Chem. Soc. Perkin Trans. II* **1986**, 1765).
- other salts are accessible through ion exchange (ex. ClO_4^-, $N(NO_2)_2^-$, $C(NO_2)_3^-$)

Synthesis - DHAT Salts



DHAT• HNO_3
DHAT• $2HNO_3$

- high heats of formation of the ring system
- unfortunately, the salts surveyed are impact sensitive and thermally unstable
- DROPPED FROM CONSIDERATION

CONCLUSIONS

- Several candidate molecules have been successfully synthesized and screened for the three programs under IHPRPT (e.g. DAAOF, BNNII, HCO, DAAF)

- Other candidate molecules are very close to being synthesized (e.g. SPIRO, NBDNT, BON), or the synthetic routes are being developed to optimize yields (ADNT)

- Find suitable replacements for the materials which exhibit poor sensitivity characteristics (esp. ADHTDN, TATFO, various furazan derivatives)